

# Adsorptive removal of aromatic organosulfur compounds over the modified Na-Y zeolites

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## Abstract

The adsorptive removal of organosulfur compounds including dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) on the various ion-exchanged Na-Y zeolites (with single  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$  and the combined  $\text{Cu}^{2+}$ – $\text{Zn}^{2+}$ ,  $\text{Zn}^{2+}$ – $\text{Nd}^{3+}$ ,  $\text{Ni}^{2+}$ – $\text{Nd}^{3+}$ ) in the model systems (the *n*-octane solutions of sulfur compounds and in some cases with small fraction of benzene/toluene) has been systematically compared. The pre-oxidation of the sulfur compounds together with adsorption procedure over Ag-Y and CuZn-Y adsorbents and the solo-oxidation of the sulfur compounds without adsorption were also performed for comparison. It was observed that the desulfurization efficiency follows the order of direct adsorption > oxidation-adsorption > direct-oxidation. The CuZn-Y was found to be a promising competitor to Ag-Y in terms of the desulfurization performance, and the former is more stable than the latter. The influence of various parameters on desulfurization of Ag-Y and CuZn-Y was investigated. The characterization results of the fresh and used samples provide insights into the characteristics of various adsorbents and the sort of interactions between the adsorbed sulfur compounds and the exchanged metal ions. A full regeneration of used Ag-Y can be achieved by air-calcination at 450 °C.

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## 1. Introduction

Recently, increasing attention has been paid to the environment issue caused by sulfur compounds in transportation fuels which is the main source of  $\text{SO}_x$  in air [1]. The U.S. Environmental Protection Agency (EPA) put forward new requirements that the sulfur content of gasoline must be reduced from the current value of 300 ppm to 30 ppm and that of diesel fuel from 500 ppm to 15 ppm by 2006 [2,3]. On the other hand, in case gasoline and diesel oil will be used for fuel cells, the sulfur level should be further reduced in order to prevent the re-forming and electrode catalysts from being poisoned by even the trace of sulfur-containing species [4,5].

Conventional hydrodesulfurization (HDS) process has been widely used to remove sulfur compounds from the liquid fuels [6,7]. However, the HDS process is generally operated at high temperature and pressure, which decreases the octane number of fuels [8]. The HDS process is effective to remove thiols, sulfides and disulfides, but it is difficult to remove thiophene, benzothiophene (BT), dibenzothiophene (DBT) and their derivatives (most importantly, 4,6-DMDBT) [9]. Therefore, it is necessary to develop non-HDS methods to meet the new standard of fuels [10]. Many new methods/processes have been developed for the purpose, including oxidation [11–17], extraction [18], adsorption [19–36], microwave-assisted desulfurization [37], etc. Among these processes the adsorption approach is rather attractive, because it does not need to consume  $\text{H}_2$  and can be operated at ambient or rather low temperature and pressure. Yang and his co-workers [20,21,23,24,30,35] reported that the transition metal ion-exchanged zeolite Y prepared by using vapor phase and solid

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state ion exchange techniques can selectively adsorb sulfur compounds from commercial fuels with high desulfurization capacities. McKinley and Angelici [25] reported that silver salts adsorbed on amorphous silica and mesoporous SBA-15 can be used to extract DBT and 4,6-DMDBT from a simulated petroleum feedstock. Song and co-workers [5,19,20,26,28] reported the transition metal ion-exchanged Y zeolites for the selective adsorption of sulfur compounds in the model and real fuels. The Ce-exchanged Y zeolite exhibited a higher sulfur adsorption capacity via the direct sulfur–adsorbent (S–M) interaction. Xue et al. [27] observed that the  $\text{Ag}^+$ ,  $\text{Cu}^+$  or  $\text{Ce}^{3+}$  ion-exchanged Y zeolites exhibited high adsorptive capacities in a model solution of hydrodesulfurized gasoline with very low sulfur concentration.

From the previous investigations one can see that the sulfur compounds can be effectively removed by adsorption over certain metal ion-exchanged Y zeolites, which established a new approach to deep desulfurization of fuels. Practically, adsorption means has been widely used in the environmentally friendly applications [31]. Note that the sort and content of sulfur compounds in these applications are rather different, and moreover, the media in which adsorption occurs also varied largely from one case to another. It is difficult to make a parallel comparison between different adsorption systems. In the present study, we first prepared the purified Na-Y by washing and repeated  $\text{Na}^+$  ion-exchanging (6 times) to eliminate impurities and other exchangeable cations. Then we fabricated a series of ion-exchanged Na-Y zeolites (with single  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$  and the combined  $\text{Cu}^{2+}$ – $\text{Zn}^{2+}$ ,  $\text{Zn}^{2+}$ – $\text{Nd}^{3+}$  and  $\text{Ni}^{2+}$ – $\text{Nd}^{3+}$ ), and adopted a model system, namely, the *n*-octane solutions with certain concentration of sulfur compounds, to study the efficiency of adsorptive desulfurization. The present study on the adsorption behaviors of the aromatic sulfur compounds such as DBT and 4,6-DMDBT over various modified Y zeolites provides an insight into the interactions between these sulfur compounds and the adsorbents, useful for further development of desulfurization technology. Influences of various parameters including initial sulfur concentration, loading of exchanged metal(s), adsorption temperature and time, amount of adsorbent, and co-existing aromatic compounds such as benzene and toluene, on desulfurization efficiency were systematically investigated. Techniques such as ICP/XRF, XRD, XPS, FT-IR, UV–vis and TA-MS were adopted to characterize the modified Y adsorbents before and after use and to investigate the interaction of the sulfur compounds with different adsorbents. The regeneration of the representative adsorbent was also tried via a simple air-calcination.

## 2. Experimental

### 2.1. Preparation of the modified zeolite adsorbents

All the reagents used in the present study are analytically pure unless specially notified. Na-Y zeolite with Si/Al molar ratio of 2.2 (Wenzhou Zeolite Company) was used as the starting material. In order to get rid of the influence of

impurities and the cations other than  $\text{Na}^+$ , the raw Na-Y zeolite was first washed with distilled water under stirring, and then the washed Na-Y zeolite was ion-exchanged with aqueous solution of NaCl (3 mol/L) at 60 °C six times. After that the material was filtered, washed with distilled water and ethanol, and dried at 100 °C in air. The sample obtained is the purified Na-Y zeolite.

Zn-Y and Cu-Y zeolites were prepared by ion-exchanging the purified Na-Y zeolite with  $\text{Zn}(\text{CH}_3\text{COO})_2$  and  $\text{Cu}(\text{NO}_3)_2$  aqueous solution at 60 °C, respectively. In order to prevent  $\text{Ag}^+$  from the photo reduction to Ag, Ag-Y zeolite was prepared by ion-exchanging the purified Na-Y zeolite with  $\text{AgNO}_3$  aqueous solution in a black box at room temperature (RT). CuZn-Y zeolite was prepared by co-ion exchanging the purified Na-Y zeolite with a mixed solution of  $\text{Cu}(\text{CH}_3\text{COO})_2$  and  $\text{Zn}(\text{CH}_3\text{COO})_2$  at 60 °C. The ion-exchanging was repeated twice for a period of 2 h. After ion exchanging, the zeolite was filtered, washed with distilled water, and dried at 100 °C over night (except for Ag-Y, it was dried at RT in a dark area) and calcined at 450 °C in He or Ar atmosphere for 18 h employing a temperature ramp of 2 °C/min. ZnNd-Y and NiNd-Y were prepared similarly as CuZn-Y.

### 2.2. Pre-oxidation of sulfur compounds

For comparison purpose, DBT and 4,6-DMDBT were subjected to a pre-oxidization with 30% hydroperoxide in the presence of 12-tungstophosphoric acid (TPA) and tetrabutyl ammonium bromide at 60 °C for 2 h before adsorption.

### 2.3. Adsorptive removal of sulfur compounds

Thiophene ( $\geq 99\%$ ), DBT ( $\geq 99\%$ ) and 4,6-DMDBT (97%) were purchased from Aldrich. Several kinds of liquid feed stocks were adopted: (i) the *n*-octane solutions of DBT containing 500–1500 ppm S; (ii) the *n*-octane solutions of DBT and 4,6-DMDBT containing 500 ppm S and 2.5 wt% toluene; (iii) *n*-octane solutions of DBT and 4,6-DMDBT containing 500 ppm S and 1 wt% benzene; and (iv) a *n*-octane solution of thiophene and DBT containing 700 ppm S. The adsorption experiments were carried out using a batch method. Zeolite adsorbent (typically 1 g) was added into a certain *n*-octane solution of sulfur compound(s) (50 ml) under continuous stirring at RT to 80 °C for 1–24 h. The adsorbent was separated from the liquid phase by filtration. The total sulfur concentration in the treated solution was analyzed by an Antek sulfur analyzer of 9000 S with the detection limit of 0.5 ppm.

### 2.4. Characterization of the fresh and used adsorbents

Chemical compositions of the modified zeolite adsorbents were determined by ICP (JA-1100) or X-ray fluorescence spectroscopy (XRF). Powder X-ray diffraction (XRD) patterns were collected on a Philips X' Pert Pro diffractometer with  $\text{Cu-K}\alpha$  radiation. UV–vis diffuse reflectance spectra were recorded on a Shimadzu UV–vis spectrometer (UV-2401PC) with barium sulfate as the reference. The spectra of X-ray

photoelectron spectroscopy (XPS) were obtained on a VG ESCALAB MK II instrument with 1253.6 eV radiation (Mg K $\alpha$ ) at a setting of 10 kV and 15 mA. The binding energy (BE) of C1s (284.6 eV) was used for calibrating the BEs of the elements. FTIR spectra were recorded at RT on a VECTOR-22 FTIR spectrometer. TA-MS coupling technique (STA-449C, Netzsch, Germany) was applied to monitor the interaction between the adsorbed sulfur compounds and the adsorbents. The samples were heated up from room temperature to 600 °C at a rate of 10 °C/min in Ar. The TG/DSC profiles and the MS signals with different  $m/z$  values can be recorded concurrently.

### 3. Results and discussion

#### 3.1. The characteristics of the ion-exchanged Y zeolites

##### 3.1.1. Elemental composition

The chemical compositions of the ion-exchanged Y zeolites were summarized in Tables 1 and 2. The M/Al ratios of the modified zeolites indicate the number of metal ions exchanged to ion-exchangeable sites. It was found that the degree of ion-exchange is low for Ag-Y, and relatively high for the other modified Y zeolites. An ion-exchanging capacity (for instance, that of Ag shown in Table 2) can be increased by either increasing the concentration of AgNO<sub>3</sub> solution or decreasing the amount of Na-Y used.

##### 3.1.2. XRD

The XRD patterns of the selected metal ion-exchanged Y zeolites calcined at 450 °C are shown in Fig. 1. The framework of Y zeolite is essentially maintained after different ion-exchanging and calcination, which is similar to that reported previously [26,27]. Note that Ag<sup>+</sup> ion-exchanging has the most obvious impact on the structure of Na-Y, likely due to the significant size effect of Ag<sup>+</sup>.

#### 3.2. Adsorptive removal of sulfur compounds

##### 3.2.1. Adsorption of DBT on the modified Y adsorbents

The results are shown in Table 3. All of the modified zeolites present better adsorption performances than Na-Y zeolite without transition metal ion-exchange. Among them, the Ag-Y

Table 2

The chemical compositions of the Ag-Y adsorbents measured by XRF

Sample	Exchanged metal ion	Content of metal element (wt%)		Ag/Al (molar ratio)
		Ag	Al	
Ag-Y(I)	Ag <sup>+</sup>	3.5	12.9	0.06
Ag-Y(II)	Ag <sup>+</sup>	2.3	13.0	0.04
Ag-Y(III)	Ag <sup>+</sup>	1.8	12.7	0.04

and CuZn-Y adsorbents show higher adsorption abilities. They nearly completely removed the DBT in the solution (with a reduction of 98–99% of 500 ppm S). The promising performance is probably due to the stronger interaction between DBT and Ag<sup>+</sup> or Cu<sup>+</sup>-Zn<sup>2+</sup>. Note that the Cu-Y and Zn-Y exhibit comparatively lower performances, possibly a result of the weaker interaction between Cu or Zn cation and DBT molecule. As the Na-Y zeolite was co-exchanged with Cu<sup>2+</sup> and Zn<sup>2+</sup>, the resulting CuZn-Y (with comparable metal content) showed notably enhanced adsorption performance. There could be a synergistic effect between the Cu–Zn cations for DBT adsorption. Similar enhancement in adsorption was observed over the co-exchanged ZnNd-Y as compared with Zn-Y. On the co-exchanged NiNd-Y, however, the performance was declined, suggesting that adsorption ability is dependent on the sort of metal ion(s) exchanged and the synergy between the co-exchanged metal ions.

##### 3.2.2. The exchanged metal content in adsorbent

Table 4 shows the effect of Cu–Zn content in CuZn-Y for the removal of DBT. The adsorption capacity increases with increasing Cu–Zn content in the adsorbent. When Cu and Zn contents were increased from 1.9% and 2.1% to 4.1% and 5.5%, respectively, the sulfur reduction was enhanced from 76% to 98% (an adsorption capacity increased from 13.3 mg S/g to 17.2 mg S/g). The results indicate that the adsorption efficiency is also influenced by the metal content in the adsorbent. Note that the increase in sulfur reduction is not proportion to the increase in metal content, suggesting that the adsorption stoichiometry may vary with metal content in the adsorbent (i.e.

Table 1

The chemical compositions of various adsorbents measured by ICP

Sample	Exchanged metal ion	Content of metals (wt%)		M/Al (molar ratio)
		M	Al	
Cu-Y	Cu <sup>2+</sup>	8.0	9.3	0.32
Zn-Y	Zn <sup>2+</sup>	10.4	9.2	0.47
CuZn-Y(I)	Cu <sup>2+</sup>	4.1	8.1	0.21
	Zn <sup>2+</sup>	5.5		0.28
ZnNd-Y	Zn <sup>2+</sup>	2.2	9.4	0.10
	Nd <sup>3+</sup>	2.1		0.04
NiNd-Y	Ni <sup>2+</sup>	2.2	9.3	0.11
	Nd <sup>3+</sup>	1.9		0.04

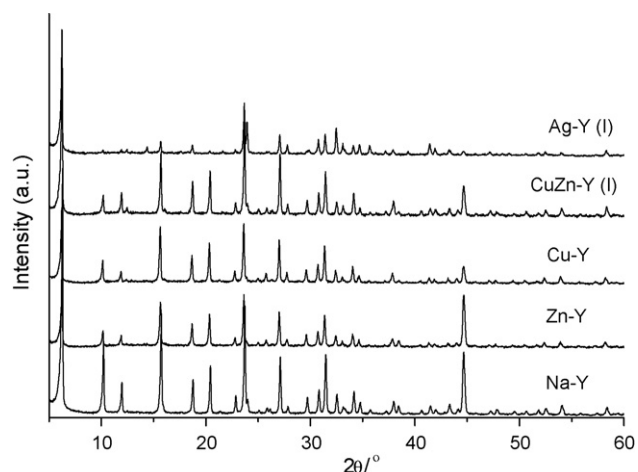


Fig. 1. XRD patterns of the modified Y adsorbents.

Table 3  
Adsorptive removal of DBT on various modified Y adsorbents<sup>a</sup>

Sample	Feed S (ppm)	Product S (ppm)	Reduction (%)	Reduction S (mg S/g)
Na-Y <sup>b</sup>	500	240	52	9.1
Na-Y	500	140	72	12.6
Ag-Y(I)	500	7	99	17.3
Zn-Y	500	75	85	14.9
Cu-Y	500	113	77	13.6
CuZn-Y(I)	500	10	98	17.2
ZnNd-Y	500	56	89	15.6
NiNd-Y	500	140	72	12.6

<sup>a</sup> Adsorption was operated at 60 °C for 24 h.

<sup>b</sup> Uncalcined sample.

not every exchanged site is accessible to DBT especially at high degree of ion-exchange). On the other hand, the effect of Ag content in Ag-Y on the removal of DBT is not so obvious. Table 5 shows that the sulfur adsorption is slightly increased as the Ag content was increased from 1.7 wt% to 3.5 wt%.

The faujasite type zeolite has one of the most open silicate frameworks in zeolite family. Takaishi studied the distribution of Na<sup>+</sup> ions in the faujasite type zeolite, and pointed out that there are different kinds of Na<sup>+</sup> sites at the hexagonal prism (I, I'), the sodalite cage (II, II', II''), and around the supercage (III, III') [38]. The affinity to a cation varies with the location of sites. The cation affinity declines in the order of site I (I'), site II (II', II''), and site III' (III). In other words, the Na<sup>+</sup> cations at sites I and I' are more difficultly exchanged by guest cations, while those at sites III and III' are more easily exchanged. With low degree of ion-exchange, such as in the case of Ag-Y, Ag<sup>+</sup> would preferentially exchange with Na<sup>+</sup> at sites III and III', and the Ag<sup>+</sup> ions at these sites are essentially accessible to sulfur compounds.

With increasing loading of guest mixed cations such as in the case of CuZn-Y, a certain fraction of Na<sup>+</sup> at sites II can be exchanged. The exchanged cations at these sites may not be fully accessible for DBT to have a direct  $\sigma$ -coordination/ $\pi$ -complexing. Note that the Na-Y itself without guest exchanged cation(s) also showed certain degree of sulfur reduction (Table 3). It is thought that besides the direct interaction between the exchanged cation(s) and the aromatic sulfur compounds, the presence of electrostatic field in the supercages of Y zeolite due to the distribution of Na<sup>+</sup> and exchanged cation(s) (Ag<sup>+</sup> in particular, due to its significant polarizability and size effect) may have an “additional” capture effect on the sulfur species. Such effect becomes significant at high sulfur concentration. This may account for the lack of dependence of DBT on the Ag<sup>+</sup> loading (Table 5, Ag-Y(I) vs. Ag-Y(III)); and

Table 4  
The effect of exchanged Cu–Zn loading on adsorption of DBT

Sample	Feed S (ppm)	Product S (ppm)	Reduction (%)	Reduction S (mg S/g)
CuZn-Y(I)	500	10	98	17.2
CuZn-Y(II)	500	120	76	13.3

CuZn-Y(I): see Table 1; CuZn-Y(II): Zn<sup>2+</sup>: 2.1 wt%, Cu<sup>2+</sup>: 1.9 wt%.

Table 5  
The effect of exchanged Ag loading on adsorption of DBT<sup>a</sup>

Sample	Feed S (ppm)	Product S (ppm)	Reduction (%)	Reduction S (mg S/g)
Ag-Y(III)	500	8	98.4	17.2
Ag-Y(I)	500	7	98.6	17.3

<sup>a</sup> Adsorption conditions: at 60 °C for 24 h, 1 g adsorbent.

also explain the measured adsorption capacity can be beyond the amount of exchanged cation. Our data recently acquired on the CuZn-MCM-41 (with more spacious channels and similar Cu–Zn loading) indicated that the adsorption ability of DBT over the CuZn-MCM-41 was notably lower than that on the CuZn-Y, possibly owing to the lack of the capture effect of supercages in Y zeolite.

### 3.2.3. Adsorption temperature

Fig. 2 shows the effect of adsorption temperature on sulfur removal over Ag-Y with an initial sulfur concentration of 1200 ppm. After adsorption at 20 °C, the sulfur content in the solution is 140 ppm, and the corresponding sulfur reduction is 37.2 mg S/g. As temperature was increased to 40 °C, the sulfur content after adsorption is 50 ppm. This indicates that there is activation energy for adsorption process (mainly for DBT diffusion). The molecule diffusion was accelerated by increasing adsorption temperature. As temperature reached 60 °C, the sulfur reduction reached the maximum. A slight decrease in sulfur adsorption was observed at 80 °C, possibly due to some desorption of DBT at higher temperature.

### 3.2.4. Initial sulfur concentration

As shown in Fig. 3, under the same conditions, the residual sulfur content after adsorption increases with increasing initial sulfur concentration. However, the overall sulfur reduction on the basis of per mass of adsorbent increases from 17.5 mg S/g to 44.9 mg S/g as the initial sulfur content was increased from

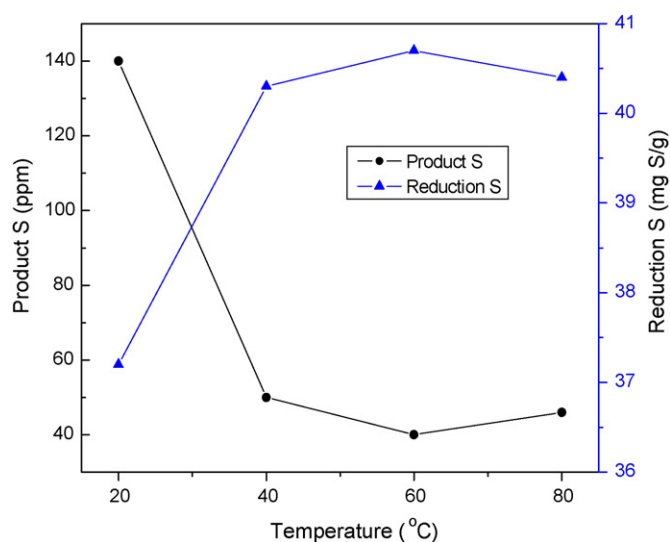


Fig. 2. The effect of temperature on DBT adsorption over Ag-Y(I). Adsorption time: 24 h, adsorbent weight: 1 g, initial S concentration: 1200 ppm.

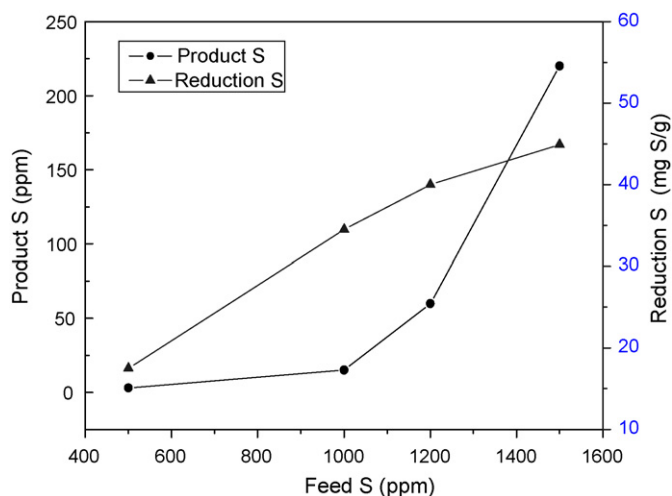


Fig. 3. The effect of initial sulfur concentration on S reduction over Ag-Y(II). Adsorption time: 1 h, temperature: 60 °C, adsorbent weight: 1 g.

500 ppm to 1500 ppm. The sulfur reduction becomes flat at higher initial S concentrations.

### 3.2.5. Adsorption time

Fig. 4 illustrates that DBT can be removed in large amount in the first 30 min (from 1500 ppm in the feed to 300 ppm in the product), and the sulfur reduction reaches 42 mg S/g. The residual sulfur concentration is further decreased to ca. 220 ppm (reduction  $S = 45$  mg S/g) after 1 h adsorption and keeps almost unchanged with extended period of adsorption. It seems that the adsorption of DBT can readily reach the equilibrium over the Ag-Y adsorbent.

### 3.2.6. Amount of adsorbent

Fig. 5 shows that the residual sulfur concentration decreases with increasing the amount of adsorbent used. When the amount of adsorbent is increased from 0.2 g to 0.5 g, the product sulfur content is reduced from 890 ppm to 480 ppm (the initial sulfur content = 1500 ppm); and the sulfur reduction

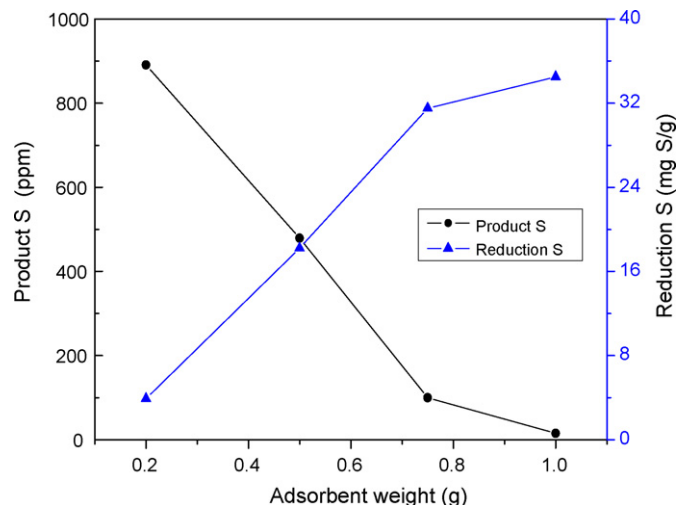


Fig. 5. The effect of adsorbent weight on S reduction over Ag-Y(II). Temperature: 60 °C, time: 1 h, initial S concentration: 1500 ppm.

increases from 3.9 mg S/g to 18.2 mg S/g. As the adsorbent amount is further increased to 1.0 g, the product sulfur content is reduced to 15 ppm and the corresponding sulfur reduction reaches 34.5 mg S/g.

### 3.3. Adsorption of different sulfur compounds on Ag-Y and CuZn-Y

The above studies concentrated on the removal of DBT over Ag-Y and other modified Y adsorbents. The influence of the operating parameters on the adsorptive removal of DBT has also been investigated. The study on adsorptive removal of other sulfur compounds over the two representative adsorbents (Ag-Y and CuZn-Y) was also fulfilled. The experiments were carried out at the following conditions: 50 ml solution + 1 g adsorbent, at 60 °C for 5 h.

First, the effect of co-presence of thiophene and DBT on the adsorption performance of Ag-Y was studied. Table 6 indicates that the sulfur content can be effectively reduced (from

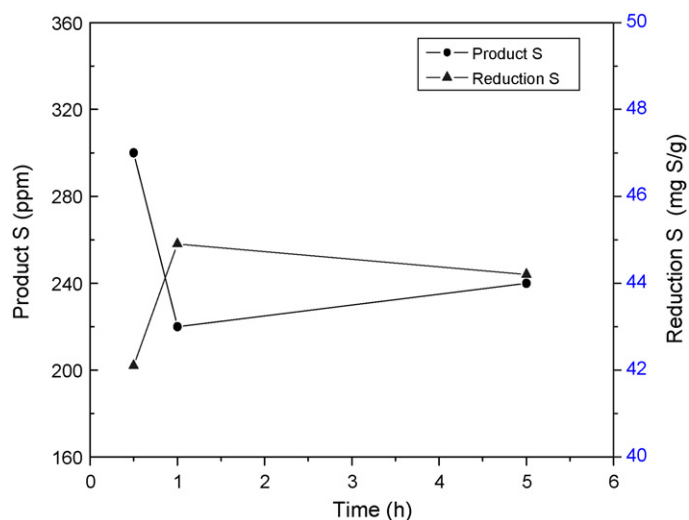


Fig. 4. The effect of adsorption time on S reduction over AgY(II). Temperature: 60 °C, initial S concentration: 1500 ppm, adsorbent weight: 1 g.



Table 6  
Adsorption of various sulfur compounds over Ag-Y(II)

Feed S (ppm)	Product S (ppm)	Reduction (%)	Reduction S (mg S/g)
700 (400 DBT + 300 thiophene)	22	97	23.8
500 (4,6-DMDBT)	3	>99	17.4
500 (DBT) + 2.5% toluene	119	76	13.4
500 (DBT) + 1% benzene	89	82	14.4
500 (4,6-DMDBT) + 1% benzene	64	87	15.3
500 (4,6-DMDBT) + 1% benzene, pre-oxidation	127	75	13.1

700 ppm in the feed to 22 ppm in the product). Table 6 also reveals that the adsorptive removal of 4,6-DMDBT on Ag-Y is as effective as that of DBT. Little steric effect of 4,6-dimethyl group on adsorption performance implies that the predominant interaction between 4,6-DMDBT and Ag<sup>+</sup> site is the  $\pi$ -complexation.

When 1% of benzene or 2.5% of toluene was added into the solution of DBT, the adsorption performances were reduced accordingly, with the sulfur reduction of 82% and 76%, respectively (Table 6). It seems that there is a competitive adsorption (via similar  $\pi$ -complexing) between benzene or toluene and DBT. As 1% of benzene was added into the 4,6-DMDBT solution, a decrease in adsorption performance was also observed, but not as much as that in the case of the DBT solution with 1% of benzene. This is understandable since the electron density of the ring of 4,6-DMDBT is higher than that of DBT, thus the  $\pi$ -complexation between 4,6-DMDBT and Ag<sup>+</sup> can be stronger than that between DBT and Ag<sup>+</sup>, favorable for the adsorption of 4,6-DMDBT. On the other hand, if 4,6-DMDBT was pre-oxidized with 30% hydroperoxide in the presence of 12-tungstophosphoric acid (TPA) and tetrabutyl ammonium bromide prior to adsorption, the adsorption performance was declined (Table 6). The oxidative desulfurization (ODS) is an effective approach to sulfur reduction. The ODS process is also usually adopted with adsorption or extraction process. Al-Shahrani et al. reported the desulfurization of diesel via the H<sub>2</sub>O<sub>2</sub> oxidation of aromatic sulfides using a tungstate catalyst [16]. By combining ODS and methanol extraction, the sulfur level in a commercial diesel can be significantly reduced. In the present study, the pre-oxidation of DBT and 4,6-DMDBT to the corresponding sulfone compounds can modify the structural configuration as well as the polarity of DBT and 4,6-DMDBT molecules. Therefore, the adsorption behavior of the sulfur-containing species is tunable over the modified Y zeolites. Due to the presence of S=O bonds in the sulfones (the oxidized DBT and 4,6-DMDBT), the steric effect of the two methyl groups to the sulfur atom in 4,6-DMDBT is declined, and the oxygen atoms may directly coordinate with the exchanged cations via  $\sigma$ -interaction. On the other hand, because of the existence of S=O bonds in the sulfone compounds, the electron density of ring is decreased, which in turn can possibly weaken the  $\pi$ -complexation between the sulfone species and the ion-exchanged cations. The data of Table 6 suggest that the O–M interaction between sulfone and Ag<sup>+</sup> is not considerably enhanced via the pre-oxidation treatment.

Table 7  
Adsorption of different sulfur compounds over CuZn-Y(I)

Feed S (ppm)	Product S (ppm)	Reduction (%)	Reduction S (mg S/g)
700 (400 DBT + 300 thiophene)	36	95	23.3
500 (4,6-DMDBT)	<3	>99	17.5
500 (DBT) + 2.5% toluene	104	79	13.9
500 (DBT) + 1% benzene	134	73	12.8
500 (4,6-DMDBT) + 1% benzene	32	94	16.4
500 (DBT), pre-oxidation	308	38	6.7
500 (4,6-DMDBT), pre-oxidation	190	62	10.9

Although Ag-Y showed the promising performance for the removal of DBT and 4,6-DMDBT, it is not very stable for practicable use. Table 7 indicates that the adsorption performances of various sulfur compounds obtained on CuZn-Y are almost identical to those obtained on Ag-Y. In the case of 4,6-DMDBT, CuZn-Y also performs very well, implying that there is effective  $\pi$ -complexation between 4,6-DMDBT and the Cu–Zn cations. Similarly, co-presence of benzene and toluene in the adsorption system brings about competitive adsorption on the adsorbent, lowering the adsorption efficiency of DBT or 4,6-DMDBT. Note that the pre-oxidation of DBT and 4,6-DMDBT caused significant reduction in adsorption performance, suggesting that the  $\pi$ -complexing between the sulfone compounds and the CuZn-Y could be remarkably weakened.

The effect of oxidative removal of sulfur compounds was examined, and the results are presented in Table 8. The oxidation process can eliminate certain amount of sulfur compounds from the oil phase, but the reduction is small. Overall, the effectiveness of desulfurization of DBT and 4,6-DMDBT over CuZn-Y and Ag-Y follows the order of direct adsorption > oxidation-adsorption > oxidation.

### 3.4. Characterization of the fresh/used adsorbents

#### 3.4.1. XPS

The XPS measurement over the representative sample of Ag-Y (II) before and after DBT adsorption is presented in Table 9. After adsorption, the binding energies of O1s, Si2p and Al2p are almost unchanged while that of Ag3d is slightly decreased, probably as a result of electron transfer from the adsorbed DBT to the exchanged Ag<sup>+</sup> via  $\pi$ -complexation.

#### 3.4.2. UV–vis

The UV–vis spectra of the modified CuZn-Y and Zn-Y adsorbents before and after DBT adsorption are shown in Fig. 6. After adsorption, the adsorbents show two shoulders in the

Table 8  
Oxidation of sulfur compounds without adsorption

Feed S (ppm)	Product S (ppm)	Reduction (%)	Reduction S (mg S/g)
500 (DBT)	362	28	4.8
500 (4,6-DMDBT)	292	42	7.3
500 (DBT) + 1% benzene	342	32	5.5
500 (4,6-DMDBT) + 1% benzene	237	53	9.2

Table 9

The XPS results of the Ag-Y(II) adsorbent before and after DBT adsorption

Sample	O1s	Si2p	Al2p	Ag3d
B.E. (eV)				
Before adsorption	531.4	102.4	74.2	368.8
After adsorption	531.4	102.3	74.1	368.5

range of 240–350 nm and an intensive band at ca. 235 nm. These are the CT bands between DBT and the exchanged metal ions, showing the evidence of the interactions. It is hard to discriminate the type of interaction, namely,  $\pi$ -complexation or S–M interaction in the UV–vis spectra.

### 3.4.3. IR

The IR measurement of the fresh and adsorbed Ag-Y zeolite provides additional insight into the adsorption of sulfur compound on Ag-Y, and the results are shown in Fig. 7. It is observed that except for the IR bands of the adsorbent itself, there are a few distinguishable new bands appearing in the

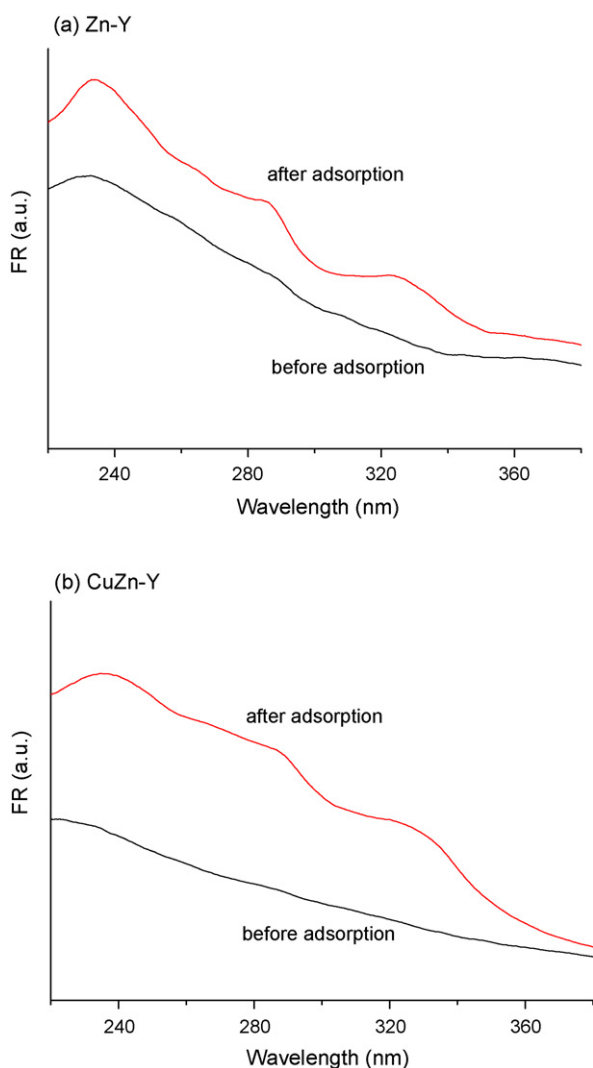


Fig. 6. UV–vis spectra of (a) Zn-Y and (b) CuZn-Y(I) adsorbents before and after DBT adsorption.

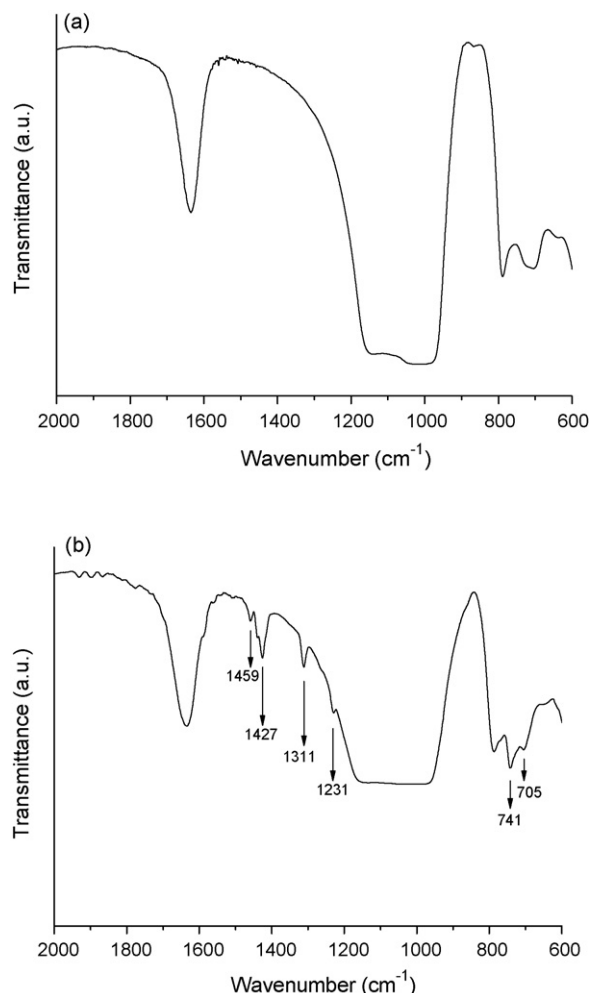


Fig. 7. IR spectra of the Ag-Y(II): (a) before and (b) after DBT adsorption.

range of 1200–1500  $\text{cm}^{-1}$  after adsorption. These bands are close to the characteristic bands of the free DBT molecule, suggesting that DBT is essentially molecularly adsorbed on the adsorbent, similar to the DBT adsorption on alumina and zirconia reported by Busca and co-workers [39]. There is a notable shift (741 and 705  $\text{cm}^{-1}$  in adsorbed DBT with respect to 755 and 722  $\text{cm}^{-1}$  in free DBT) in the out-of-plane deformation modes of adsorbed DBT on Ag-Y in the range of 700–800  $\text{cm}^{-1}$ , suggesting that there are adsorbed DBT side on the exchanged  $\text{Ag}^+$  ( $\pi$ -complexation) [39]. The adsorption of DBT over Ag-Y in our model system is similar to the situations reported by Yang and co-workers [20,21,23,24,30].

### 3.4.4. TA-MS

The TA-MS coupling technique was adopted to study the interactions between the adsorbed sulfur compound and adsorbents. When the samples (after adsorption) were linearly heated up in Ar atmosphere, desorption/decomposition of the adsorbed sulfur compound occurs, and the products can be concurrently monitored by the on-line mass spectrometer. In this study, the signal of  $m/z = 64$  corresponding to  $\text{SO}_2$  fragment was monitored in the temperature programmed process. It is thought that the more strongly interacted sulfur species has

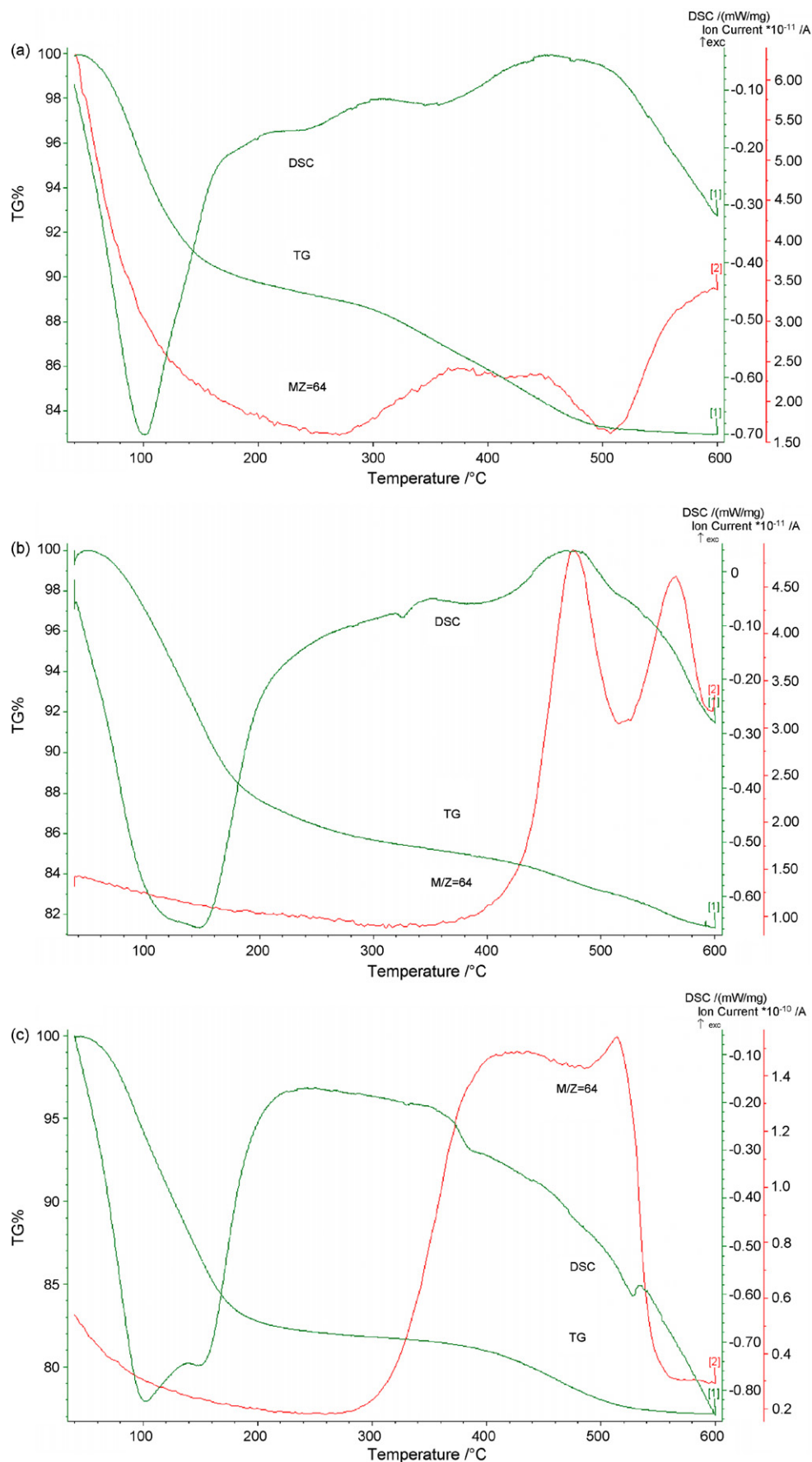


Fig. 8. TG-DSC profiles and MS signal of  $m/z = 64$  obtained on the used adsorbents. (a) Ag-Y(II), (b) CuZn-Y(I), and (c) Zn-Y.



Table 10

Sulfur reduction on the fresh and regenerated Ag-Y(II)<sup>a</sup>

Sample	Feed S (ppm)	Product S (ppm)	Reduction (%)	Reduction S (mg S/g)
Fresh	500	<3	>99	>17.5
Regenerated	500	<3	>99	>17.5

<sup>a</sup> Adsorption conditions: at 60 °C for 1 h, 1 g adsorbent.

higher thermal stability, corresponding to dissociative desorption at higher temperatures with intensive MS signal of  $m/z = 64$ . Fig. 8 showed that on the Ag-Y, there is plenty of DBT desorbing at temperatures of 100–500 °C. The desorption of DBT is mainly non-dissociative (in molecular form), since the MS signal ( $m/z = 64$ ) is rather weak. The decomposition of strongly adsorbed DBT at temperatures >500 °C on Ag-Y, but the MS signal of  $m/z = 64$  is comparatively weak. Since the Ag–S interaction is rather strong, the dissociated S species as well as some C fragments may retain on the Ag-Y surface. The desorption of DBT on CuZn-Y is somehow different. There are more DBT molecules dissociatively desorbing at temperatures >450 °C, and greater amount of SO<sub>2</sub> was released into the gas phase. There are two separated MS signals of  $m/z = 64$ , possibly corresponding to the DBT molecules associated with the two kinds of metal ions. On the Zn-Y, the dissociative desorption of DBT is almost completed in the temperature range of 400–560 °C, accompanying with a significant release of SO<sub>2</sub>. It is speculated that the DBT molecules of  $\pi$ -complexation as well as those captured by electrostatic field are weakly adsorbed, and easily desorbed in molecular form (the non-dissociative desorption); while the DBT molecules via the S–M bonding are more strongly adsorbed, and mainly undergo dissociative desorption.

Previous investigations on the adsorptive removal of sulfur compounds over certain adsorbents indicated that the sulfur compounds can be removed either by the formation of the S–M bonds [5,19,22,26,28] or by the  $\pi$ -complexation [20,21,23,24,30,35]. The type of interaction could be influenced by several critical variables such as the nature and concentration of sulfur compound, the type of exchanged metal ion, the co-existing molecule and the adsorption medium. The previous [27] and the present study revealed that the interaction can change considerably upon the type of metal ions as well as sulfur compounds. Co-presence of  $\pi$ -complexing and S–M bonding over a specific adsorbent (for instance the DBT on Zn-Y in the presence case) is also highly possible. Due to the competitive adsorption of co-existing aromatics such as benzene and toluene, both  $\pi$ -complexing and S–M bonding of sulfur compounds can be hindered to some degree (Tables 6 and 7).

### 3.5. Regeneration of the used adsorbent

The used Ag-Y adsorbent was subjected to air-calcination at 450 °C for 6 h. Table 10 indicated that the sulfur reduction of the regenerated Ag-Y is identical to that of the freshly prepared one. Air-calcination of used Ag-Y at lower temperatures (e.g. at 350 °C) would cause incomplete decomposition of the

adsorbed sulfur species, resulting in declined adsorption performance. This is understandable in terms of the TA-MS results (Fig. 8a).

## 4. Conclusion

In the present study, the adsorptive removal of aromatic sulfur compounds including DBT and 4,6-DMDBT on various ion-exchanged Na-Y zeolites (with single Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>+</sup> and the combined Cu<sup>2+</sup>–Zn<sup>2+</sup>, Zn<sup>2+</sup>–Nd<sup>3+</sup>, Ni<sup>2+</sup>–Nd<sup>3+</sup>) in the model systems (the *n*-octane solutions of sulfur compounds with or without small fraction of benzene/toluene) has been systematically studied. The pre-oxidation of the sulfur compounds together with adsorption procedure over Ag-Y and CuZn-Y adsorbents and the solo-oxidation of the sulfur compounds without adsorption were also performed for comparison. The desulfurization effectiveness follows the order of direct adsorption > oxidation-adsorption > solo-oxidation. The Ag-Y and CuZn-Y are very capable of removing DBT and 4,6-DMDBT via adsorption approach. The effects of operating parameters such as initial sulfur concentration, exchanged metal loading, adsorption temperature and time, amount of adsorbent used and co-existing aromatic compounds on desulfurization were investigated and the optimized conditions were applied for other adsorption systems. The co-exchanged CuZn-Y adsorbent is a promising competitor to Ag-Y according to the deep desulfurization performance for DBT and 4,6-DMDBT as well as the higher stability of adsorbent. Various characterizations have been conducted to study the properties of the modified Y zeolites and the adsorbed sulfur species for understanding the adsorption mechanism. The adsorption performance of a used adsorbent (Ag-Y) can be fully recovered by air-calcination at 450 °C.

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